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Photoluminescence oscillations in porous alumina films

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The dominant oscillation shown in the laser-excited photoluminescence spectrum of the porous alumina film can be ascribed to the interference within a Fabry-Pérot optical cavity where the separation between two neighboring oscillations is highly sensitive to the film's thickness and refractive index. The method, designated as photoluminescence oscillation, endows photoluminescence spectrum with another dimension and results in a nondestructive method for the measurement of the thickness and refractive index with a high resolution. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2390645]

Thickness monitoring is an indispensable growth control in chemical vapor deposition. Moreover, thickness is also an important parameter in material characterization. There are many methods for thickness measuring. Atomic force microscope (AFM), scanning electron microscope (SEM), and transmission electron microscope (TEM) are common devices to obtain thickness data, but making a TEM sample is somewhat a tedious work. Other measuring methods include spectral reflectance or transmittance, x-ray diffraction, and ellipsometry. However, the above methods have restrictions. For example, spectral transmittance can only be used to measure transparent substrate, and ellipsometry is not suitable for measureing porous films because the effective refractive index varies with the porosity of porous films.

We report a photoluminescence (PL) study on the porous alumina films.[1–6] The study reveals that the evident oscillations exposed on the laser-excited PL spectrum, designated as PL oscillation, contains information related to the film thickness and effective refractive index. Detailed analysis indicated that this structure sensitivity could be used for measuring thickness and refractive index. It should be noted that a similar explanation on the PL oscillation in porous Si has been reported previously.[7]

Porous alumina film with periodic nanopore lattice is widely used as a template or mask in the fabrication of mesostructures.[8–12] It also acts as an insulator host to sustain the functional material on many occasions. Moreover, porous alumina film can emit strong blue light.[13,14] Thus the study is valuable in optical applications, and it is helpful in elucidating some confused explanations on luminescence spectra.

In our experiment, porous alumina film was made by anodizing Al foils (99.999%, 0.5 mm thick). After annealing under N_2 ambient at 450 °C for 4 h, Al foil was ultrasonically degreased in acetone for 5 min, and then it was electrochemically polished in a mixture solution of $HClO_4$ and C_2H_5OH with a volume ratio of 20:80. The polished Al foil was placed on the anode (Cu plate) and anodized under constant dc 40 V in 0.3*M* oxalic acid at 5 °C. A Pt wire served as the cathode. Serial samples were made with different anodizing durations ranging from 10 min to 8 h. For comparison, the unpolished Al foils were also used in anodization. The mean surface roughness was measured using AFM (NanoScope IIIa). The sample morphology was observed using a SEM (LEO 1530VP). The PL was excited by a He–Cd laser (325 nm).

We investigated two typical samples of porous alumina, which were anodized respectively from polished and unpolished Al foils. Figure 1 shows the laser-excited PL spectra of these two samples, which the spectra feature with two subbands of 2.66 (F center) and 3.06 eV (F^+ center).[13,14] However, the spectrum *b* of the polished sample is surprisingly different from that of the unpolished sample. The emission intensity presented evident oscillations in a period of about 0.095 eV. Note that polishing Al foil or not before anodizing is the only difference between the two samples. Therefore the surface roughness should be the key factor to the PL oscillation. On the other hand, using a laser to excite PL is also important in obtaining the PL oscillation.

Figure 2 shows the PL spectra of the polished samples with different thicknesses. The related parameters are listed in Table I which show two trends: (1) the oscillating period is inversely proportional to the film thickness; (2) the product of thickness and oscillation period is nearly constant, 3.8×10^5 nm meV, with an average deviation of 5.2% for all samples. This is the typical character of a plane-parallel cav-

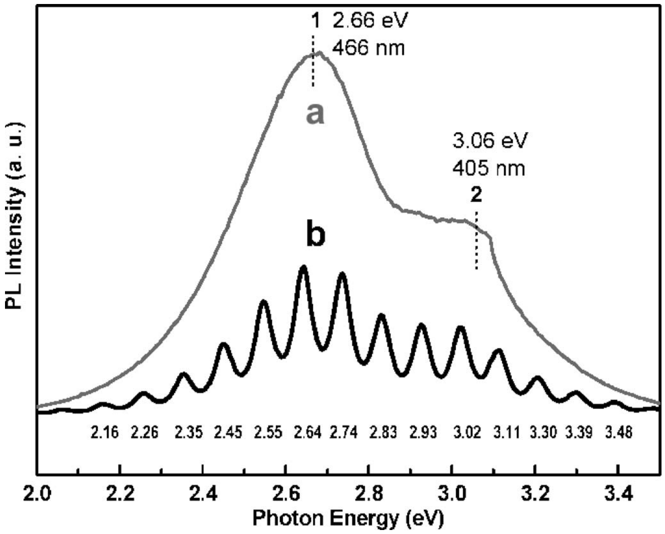

FIG. 1. PL spectra of the porous alumina films. The samples were anodized for 5 h from the unpolished Al foils [sample (a)] and 1 h from the polished Al foil [sample (b)], respectively. The surface mean roughness of the unpolished and polished Al foils were 38 and 9 nm, respectively, measured by AFM over a scan area of 3 μm^2.

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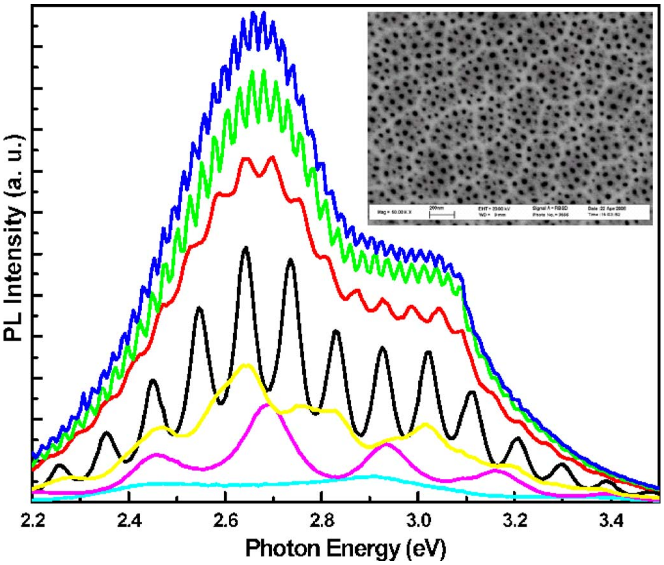

FIG. 2. (Color online) PL spectra of the porous alumina films with the same pore diameter but different thicknesses (samples 1–7, from the lower to the upper; note Table I). All samples were anodized from polished Al foils. The PL spectrum of sample 4 is also highlighted in Fig. 1 [sample (b)]. The inserted SEM image of porous alumina film indicates a porosity of 8%. The scale bar is 200 nm.

ity where the oscillation period corresponds to the difference between two longitudinal modes. Note that the pore diameter of the porous alumina is about 30 nm (insert, Fig. 2). This diameter corresponds to a cell tip (barrier layer) of about 100 nm. Therefore, the plane approximation is reasonable; i.e., the porous alumina film is a Fabry-Pérot cavity since the size of the barrier layer is much less than the wavelength of the emitting light.

The origin of the PL oscillation related to the Fabry-Pérot cavity is schematically shown in Fig. 3. We deduced that the oscillation should result from the interference between the emitting wave (1) and its round-trip reflected wave (1′). In general, the separation of longitudinal modes of a Fabry-Pérot cavity of length L reads as[15]

$$\Delta\lambda \approx \frac{\lambda^2}{2L[n-\lambda(dn/d\lambda)]}, \qquad (1)$$

where n is the refractive index of the sample of porous alumina, $dn/d\lambda$ is the material dispersion and L is the sample thickness. Note that the separation ΔE of two neighboring oscillating peaks is almost constant. This phenomenon hints that the effective refractive index of the sample should change a little for the light with photon energy ranging from 3.54 to 2.25 eV (350–550 nm); thus the material dispersion $(dn/d\lambda)$ can be treated as zero. The reliability of this supposition was also strengthened by the following facts: the band gap of alumina is much bigger than the photon energy of the measure region (2.25–3.54 eV), and the absorption coefficient is very small. With these facts, the mode spacing ΔE can be deduced from formula (1) as $\Delta E = hc/2nL$, or $nL = hc/2\Delta E$, where h is Planck's constant (6.626×10^{-34} J s), c is the speed of light (2.998×10^{8} m/s), and nL is generally defined as the optical length of the material.

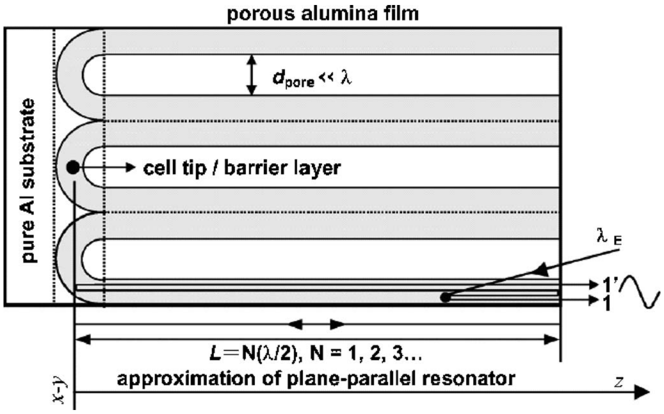

FIG. 3. Sketch of the PL oscillations due to the interference between emitting light 1 and 1′ under the approximation of plane-parallel (or Fabry-Pérot) resonator. Note that the size of the round cell tip is much less than the wavelength of emitting light.

Figure 4 shows the linear dependence between the thickness of the porous alumina films (L) and the optical lengths (nL) calculated from the data in Table I. It is valuable because the slope of the fitted line represents the refractive index of the porous alumina film, which was 1.66 in our experiment. For comparison, the Bruggeman equation[16] also gives an access to the effective refractive index n_{eff} of the complex material,

$$(1-p)\frac{n_{\mathrm{alumina}}^2 - n_{\mathrm{eff}}^2}{n_{\mathrm{alumina}}^2 + 2n_{\mathrm{eff}}^2} + p\frac{1-n_{\mathrm{eff}}^2}{1+2n_{\mathrm{eff}}^2} = 0, \qquad (2)$$

where n_{alumina} is the refractive index of the matrix phase of alumina (1.67),[17] and the porosity p is the percentage of the minor phase of the air columns (pores). Considering the structure geometry of the porous alumina film, the porosity p can be obtained from the statistic of the pore area using a top-view SEM image; in our experiment, it is typically 8% (insert, Fig. 2). These data result in an effective refractive index n_{eff} of 1.62 from the Bruggeman equation. This result matches the coefficient of average deviation of 2% to 1.66 extracted from the PL oscillation.

In conclusion, the dominant oscillations shown in the laser-excited PL spectrum of the porous alumina film can be ascribed to the interference within a Fabry-Pérot optical cavity, where the separation between two neighboring oscillations is highly sensitive to the film thickness and refractive index. Because the material dispersion $(dn/d\lambda)$ is zero under

TABLE I. Parameter dependence of the PL oscillation (the thickness was measured using SEM).

Porous alumina film		1	2	3	4	5	6	7
Anodized time	[t (min)]	10	20	30	60	120	300	480
Film thickness	[L (nm)]	8.200×10^2	1.520×10^3	2.09×10^3	3.84×10^3	6.45×10^3	1.3×10^4	1.9×10^4
Oscillation period	[ΔE (meV)]	5.0×10^2	2.4×10^2	1.9×10^2	9.6×10	5.8×10	2.6×10	2.1×10
$L\cdot\Delta E$ (nm meV)								
3.8×10^5 nm meV		4.1×10^5	3.6×10^5	3.9×10^5	3.7×10^5	3.7×10^5	3.4×10^5	4.0×10^5

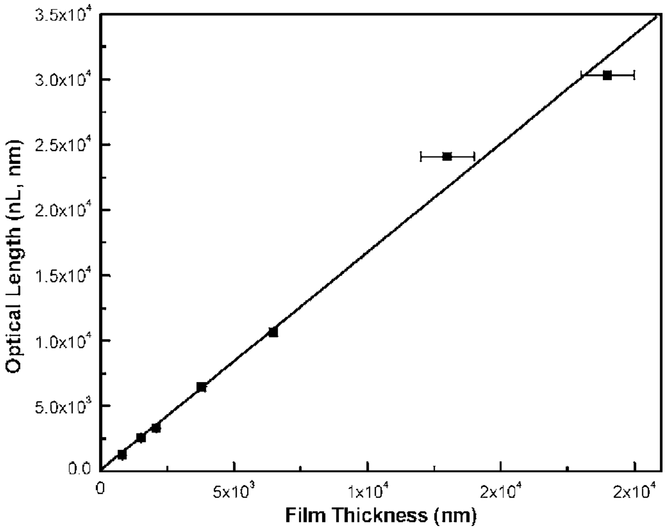

FIG. 4. Linar dependence between optical length and film thickness. The slope of the fitted line represents the effective refractive index of the sample of porous alumina film.

certain measurement conditions, the PL emission shows the intensity oscillation with equidistant subpeaks. Moreover, the effective refractive index n_{eff} can be easily extracted from the nL-L dependence. We believe that this optical phenomenon is not a special case but just structure related; that is, if the film thickness is compared with $k(\lambda/2)$ $(k=1,2,3\ldots)$, the PL oscillation will be observed. However, if $dn/d\lambda$ is far beyond zero, the PL oscillation is somewhat complex because the spaces between neighboring oscillating peaks will be different. The detailed discussion will be published elsewhere. Considering that the optical parameters are related to band energy, luminescence center, exciton, and phonon could be extracted from the PL spectrum; therefore, the elucidated PL oscillation endows PL spectrum with another dimension. It results in a nondestructive method for the measurement of the thickness and refractive index with a high resolution.

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